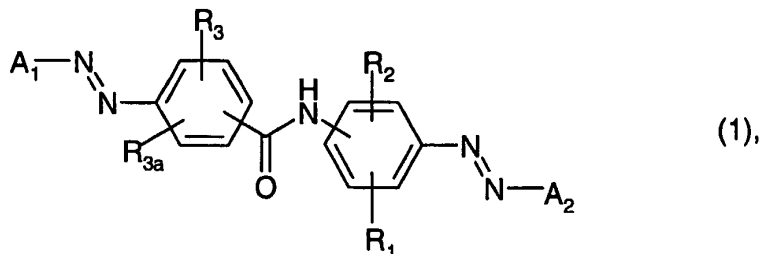


Claims

1. A compound of the formula



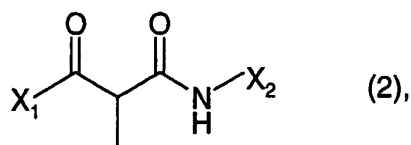
in which

R<sub>1</sub> represents hydrogen, substituted or unsubstituted C<sub>1</sub>-C<sub>8</sub>alkyl, substituted or unsubstituted C<sub>1</sub>-C<sub>8</sub>alkoxy or SO<sub>3</sub>H,

R<sub>2</sub> represents SO<sub>3</sub>H or CO<sub>2</sub>H,

R<sub>3</sub> and R<sub>3a</sub> each, independently of the other, represent hydrogen, a C<sub>1</sub>-C<sub>4</sub>alkyl group, which may be substituted or unsubstituted, halogen, hydroxy, substituted or unsubstituted C<sub>1</sub>-C<sub>4</sub>alkoxy, carboxy, NH<sub>2</sub> or NHC<sub>1</sub>-C<sub>4</sub>alkyl and each of the residues

A<sub>1</sub> and A<sub>2</sub>, independently of the other, is derived from a coupling component selected from the group consisting of  
an acetoacetylated amine of the formula



in which

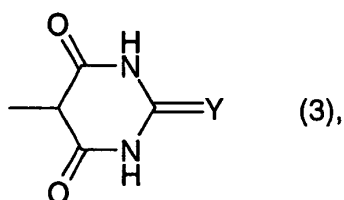
X<sub>1</sub> represents C<sub>1</sub>-C<sub>4</sub>alkyl, or phenyl which is unsubstituted or monosubstituted by C<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>1</sub>-C<sub>4</sub>alkoxy or halogen and

X<sub>2</sub> represents phenyl which is unsubstituted, mono-, di- or trisubstituted by one or two SO<sub>3</sub>H, SO<sub>2</sub>NHC<sub>1</sub>-C<sub>4</sub> alkyl groups which alkyl groups may be substituted, SO<sub>2</sub>C<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>1</sub>-C<sub>4</sub>substituted or unsubstituted alkyl, hydroxy, C<sub>1</sub>-C<sub>4</sub>alkoxy, halogen, CF<sub>3</sub>, NH<sub>2</sub>, NHCOC<sub>1</sub>-C<sub>4</sub>alkyl, NHCOOC<sub>1</sub>-C<sub>4</sub>alkyl, NHCONHC<sub>1</sub>-C<sub>4</sub>alkyl, CO<sub>2</sub>H, CONHC<sub>1</sub>-C<sub>4</sub>alkyl or NO<sub>2</sub>;

- 70 -

a 1- or 2-naphthyl residue which is unsubstituted or substituted by one or two  $\text{SO}_3\text{H}$ ,  $\text{SO}_2\text{NHC}_1\text{-C}_4\text{alkyl}$ , carboxy,  $\text{CONHC}_1\text{-C}_4\text{alkyl}$ , carboxy $\text{C}_1\text{-C}_4\text{alkyl}$  or carboxyaryl groups or a 5- or 6-membered heterocyclic ring containing 1-3 heteroatoms and which may be benzannelated and be further substituted by  $\text{C}_1\text{-C}_4\text{alkyl}$ ,  $\text{C}_1\text{-C}_4\text{alkoxy}$  or halogen and which may be attached to the NH-atom in formula (2) either via the hetero- or benzo-nucleus, in the case of benzannelated heterocycles;

a derivative of barbituric acid of the formula

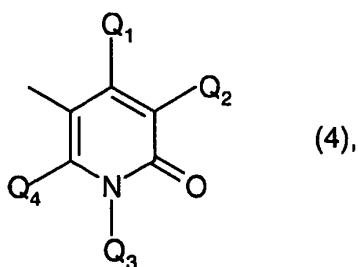


in which

Y represents O, NCN or NCONH<sub>2</sub>;

a 2,4,6-triaminopyrimidine derivative;

a pyridone derivative of the formula



in which

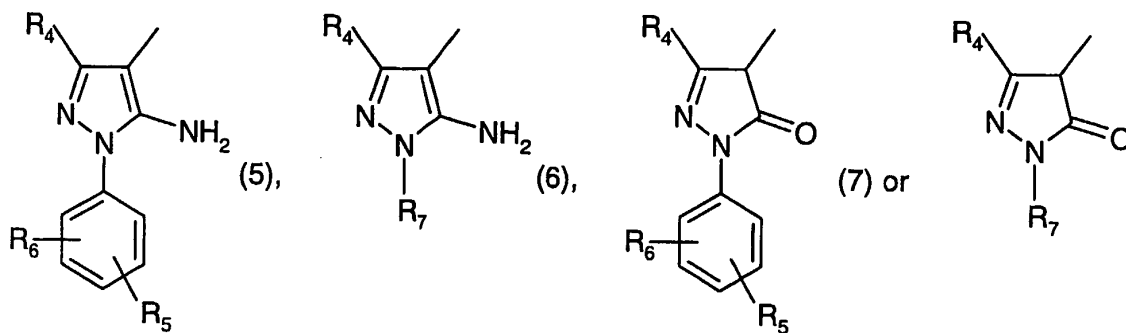
Q<sub>1</sub> represents hydrogen, hydroxy,  $\text{C}_1\text{-C}_2\text{alkyl}$ , hydroxyethyl, 2-( $\text{C}_1\text{-C}_2\text{alkoxy}$ )alkyl,  $\text{C}_1\text{-C}_2\text{alkoxy}$ , COOH, CONH<sub>2</sub> or COOC<sub>1-C2</sub>alkyl,

Q<sub>2</sub> represents hydrogen, CN, CONH<sub>2</sub>, halogen,  $\text{SO}_3\text{H}$  or  $\text{C}_1\text{-C}_2\text{alkyl}$  which is unsubstituted or substituted by hydroxy, phenyl or  $\text{SO}_3\text{H}$ ,

Q<sub>3</sub> represents hydrogen, phenyl,  $\text{C}_1\text{-C}_2\text{alkylphenyl}$ , cyclohexyl or  $\text{C}_1\text{-C}_4\text{alkyl}$  which is unsubstituted or substituted by hydroxy, CN,  $\text{C}_1\text{-C}_2\text{alkoxy}$  or  $\text{SO}_3\text{H}$  and

Q<sub>4</sub> represents hydrogen or hydroxy;

an aminopyrazole or a pyrazolone derivative of formula



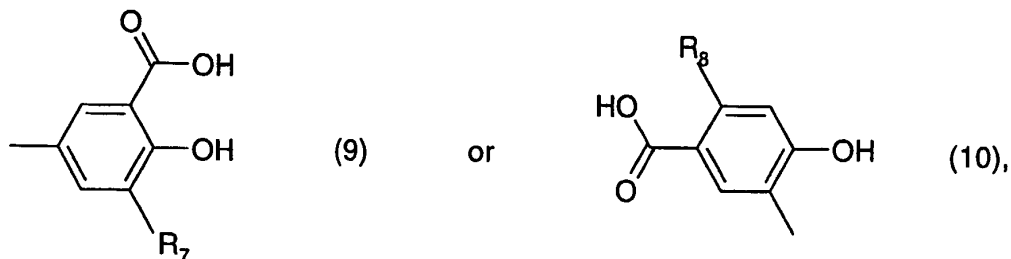
in which

$R_4$  represents hydrogen, substituted or unsubstituted  $C_1$ - $C_4$ alkyl,  $C_2$ - $C_4$ alkenyl,  $NHCO$   $C_1$ - $C_4$ alkyl or  $CO_2H$ , each

$R_5$  and  $R_6$ , independently of the other, represent hydrogen, halogen,  $C_1$ - $C_4$ alkyl,  $SO_3H$  or  $CO_2H$  and

$R_7$  represents hydrogen or  $C_1$ - $C_4$ alkyl;

a benzoic acid derivative of formula

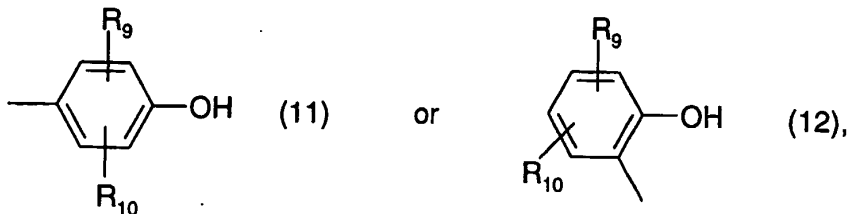


in which

$R_7$  represents hydrogen or  $C_1$ - $C_4$ alkyl and

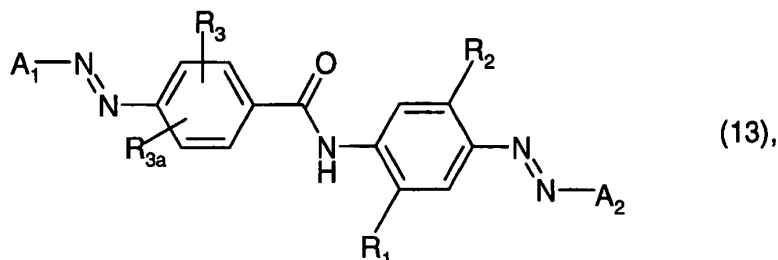
$R_8$  represents hydrogen or hydroxy or

$A_1$  and  $A_2$ , each one independently of the other, represent a phenol residue of the formula



in which

R<sub>9</sub> and R<sub>10</sub>, each one independently of the other, represent hydrogen, C<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>1</sub>-C<sub>4</sub>alkoxy, hydroxy, halogen, NH<sub>2</sub>, NHCO C<sub>1</sub>-C<sub>4</sub>alkyl, NO<sub>2</sub>, SO<sub>3</sub>H, CO<sub>2</sub>C<sub>1</sub>-C<sub>4</sub>alkyl or CONHC<sub>1</sub>-C<sub>4</sub>alkyl groups,  
with the proviso that in compounds of formula



if

R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>3a</sub> each, independently of the others, are hydrogen or SO<sub>3</sub>H, then  
A<sub>1</sub> and A<sub>2</sub> are not both a 1-phenyl or 1-sulphophenyl-3-methyl-5-aminopyrazole residue,  
or, if

R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>3a</sub> represent hydrogen and

A<sub>1</sub> is a residue of formula (9) in which

R<sub>7</sub> represents hydrogen or methyl, then

A<sub>2</sub> does not represent a 1-phenyl or 1-sulphophenyl-3-methyl- or 3-carboxy pyrazol-5-one residue

or, if

R<sub>1</sub>, R<sub>3</sub> and R<sub>3a</sub> are hydrogen and R<sub>2</sub> is SO<sub>3</sub>H and one of

A<sub>1</sub> and A<sub>2</sub> represents a 1-sulphophenyl-3-methyl pyrazol-5-one residue, then the other is not a residue of formula (11) in which both

R<sub>9</sub> and R<sub>10</sub> are hydrogen, or if

A<sub>1</sub> represents a 1-nitrophenyl-, a 1-phenyl- or an unsubstituted 3-methyl pyrazol-5-one residue,

A<sub>2</sub> is not a residue of formula (9) in which R<sub>7</sub> represents hydrogen, or if

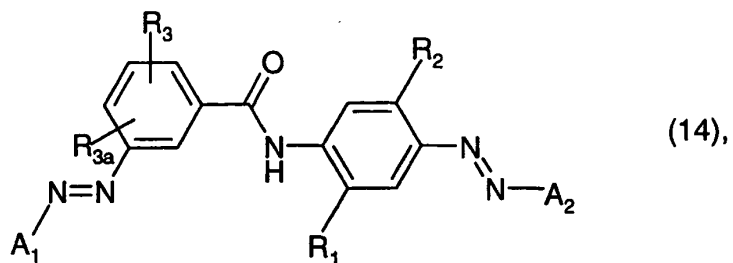
R<sub>1</sub>, R<sub>3</sub> and R<sub>3a</sub> represent hydrogen, R<sub>2</sub> is CO<sub>2</sub>H and

A<sub>1</sub> represents a residue of formula (9), in which R<sub>7</sub> is hydrogen,

A<sub>2</sub> is not a residue of formula (2) or formula (7);

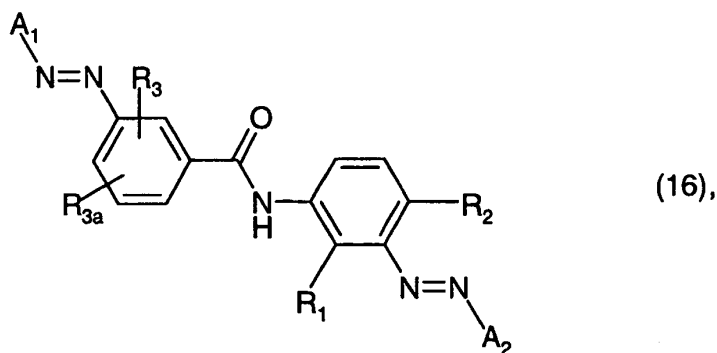
in compounds of the formula

- 73 -



if

$R_2$  represents  $\text{CO}_2\text{H}$ ,  $R_3$  represents hydroxy or methoxy and  $R_{3a}$  represents hydrogen,  
 $A_1$  and  $A_2$  do not represent residues of formulae (2) or (7) and,  
 in compounds of the formula

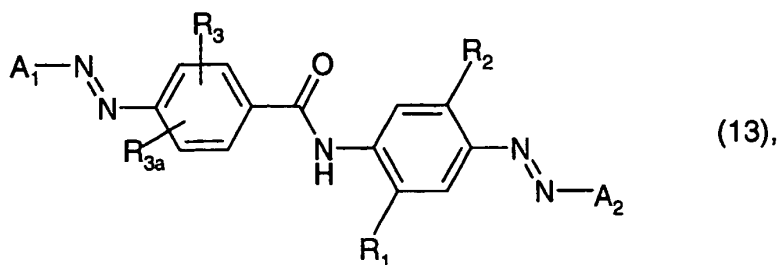


if

$R_2$  represents  $\text{SO}_3\text{H}$  and  $R_3$  and  $R_{3a}$  both represent hydrogen  
 $A_1$  and  $A_2$  are not both 2,4-dihydroxyphenyl.

2. A compound of formula (1), according to claim 1, which contains a total number of two, three or four  $\text{SO}_3\text{H}$  and/or  $\text{CO}_2\text{H}$  groups.

3. A compound of the formula



- 74 -

according to claims 1 or 2, in which

R<sub>1</sub> represents hydrogen, C<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>1</sub>-C<sub>4</sub>alkoxy or SO<sub>3</sub>H,

R<sub>2</sub> represents SO<sub>3</sub>H or CO<sub>2</sub>H,

R<sub>3</sub> represents hydrogen, a C<sub>1</sub>-C<sub>4</sub>alkyl group, halogen, hydroxy, C<sub>1</sub>-C<sub>4</sub>alkoxy, carboxy, NH<sub>2</sub> or NHC<sub>1</sub>-C<sub>4</sub>alkyl,

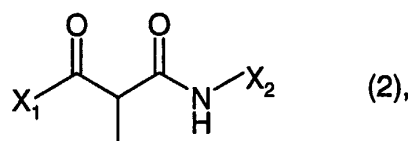
R<sub>3a</sub> represents hydrogen or NH<sub>2</sub> and

A<sub>1</sub> and A<sub>2</sub> are as defined in claim 1.

4. A compound of formula (13), according to claim 3, in which

R<sub>3</sub> and R<sub>3a</sub> both represent hydrogen and

A<sub>1</sub> and A<sub>2</sub>, each one independently of the other, is derived from a coupling component selected from the group consisting of an acetoacetylated amine of the formula



in which

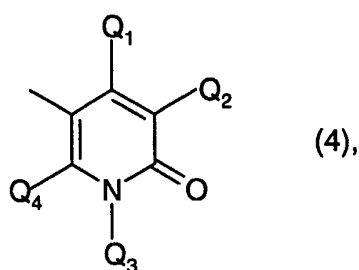
X<sub>1</sub> represents C<sub>1</sub>-C<sub>4</sub>alkyl, and

X<sub>2</sub> represents phenyl, which is unsubstituted, mono-, di- or trisubstituted by SO<sub>3</sub>H, C<sub>1</sub>-C<sub>4</sub>alkyl, hydroxy, C<sub>1</sub>-C<sub>4</sub>alkoxy, halogen or CO<sub>2</sub>H; barbituric acid or cyanoiminobarbituric acid;

2,4,6-triaminopyrimidine;

citrazinic acid;

a pyridone derivative of the formula



in which

Q<sub>1</sub> represents C<sub>1</sub>-C<sub>2</sub>alkyl,

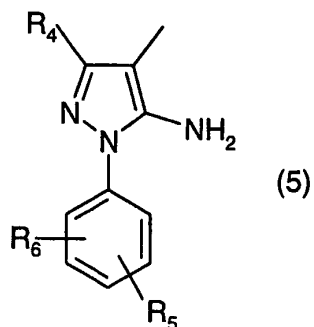
- 75 -

Q<sub>2</sub> represents CN, CONH<sub>2</sub> or CH<sub>2</sub>SO<sub>3</sub>H,

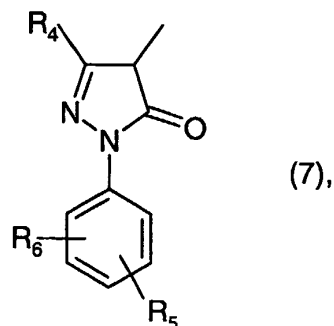
Q<sub>3</sub> represents C<sub>1</sub>-C<sub>2</sub>alkyl and

Q<sub>4</sub> represents hydroxy;

an aminopyrazole or a pyrazolone derivative of formula



or



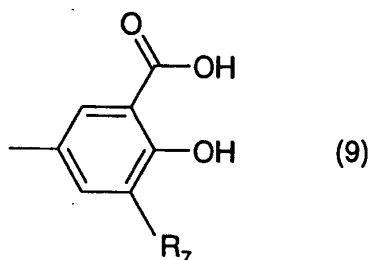
in which

R<sub>4</sub> represents C<sub>1</sub>-C<sub>4</sub>alkyl or CO<sub>2</sub>H,

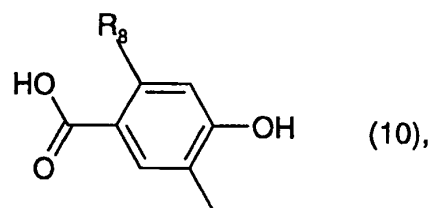
R<sub>5</sub> represents hydrogen, halogen, C<sub>1</sub>-C<sub>4</sub>alkyl, SO<sub>3</sub>H or CO<sub>2</sub>H and

R<sub>6</sub> represents hydrogen;

a benzoic acid derivative of formula



or

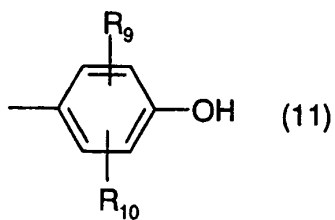


in which

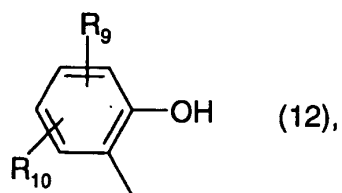
R<sub>7</sub> represents hydrogen or C<sub>1</sub>-C<sub>4</sub>alkyl and

R<sub>8</sub> represents hydrogen or hydroxy or

A<sub>1</sub> and A<sub>2</sub>, each one independently of the other, represent a phenol residue of the formula



or

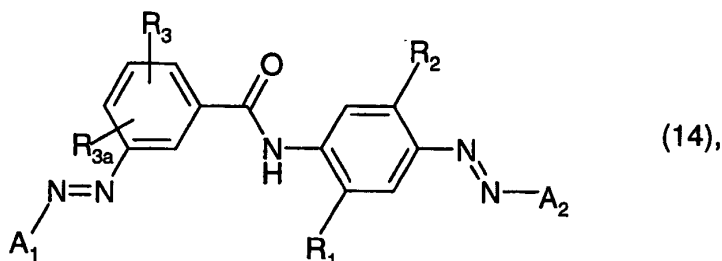


in which

R<sub>9</sub> represents hydrogen, C<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>1</sub>-C<sub>4</sub>alkoxy, hydroxy, halogen or SO<sub>3</sub>H and

R<sub>10</sub> represents hydrogen.

5. A compound of formula



according to claims 1 or 2, in which

R<sub>1</sub> represents hydrogen, C<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>1</sub>-C<sub>4</sub>alkoxy or SO<sub>3</sub>H,

R<sub>2</sub> represents SO<sub>3</sub>H or CO<sub>2</sub>H,

R<sub>3</sub> represents hydrogen, a C<sub>1</sub>-C<sub>4</sub>alkyl group, halogen, hydroxy, C<sub>1</sub>-C<sub>4</sub>alkoxy, carboxy, NH<sub>2</sub> or NHC<sub>1</sub>-C<sub>4</sub>alkyl,

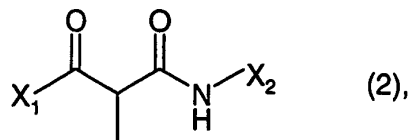
R<sub>3a</sub> represents hydrogen or NH<sub>2</sub> and

A<sub>1</sub> and A<sub>2</sub> are as defined in claim 1.

6. A compound of formula (14), according to claim 5, in which

R<sub>3</sub> and R<sub>3a</sub> both represent hydrogen and

A<sub>1</sub> and A<sub>2</sub>, each one independently of the other, is derived from a coupling component selected from the group consisting of an acetoacetylated amine of the formula



in which

X<sub>1</sub> represents C<sub>1</sub>-C<sub>4</sub>alkyl, and

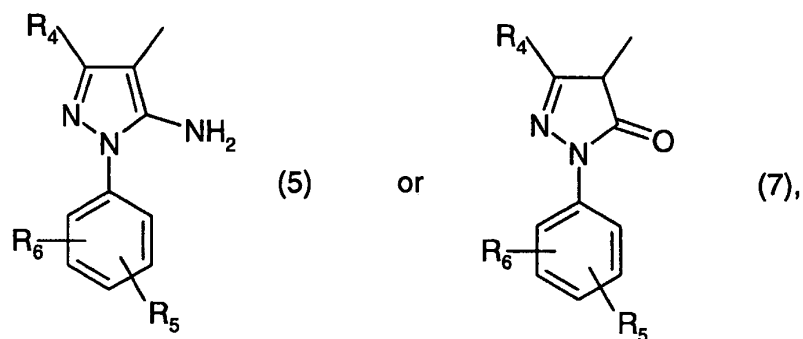
X<sub>2</sub> represents phenyl, which is unsubstituted, mono-, di- or trisubstituted by SO<sub>3</sub>H, C<sub>1</sub>-C<sub>4</sub>alkyl, hydroxy, C<sub>1</sub>-C<sub>4</sub>alkoxy, halogen or CO<sub>2</sub>H; barbituric acid or cyanoiminobarbituric acid;

2,4,6-triaminopyrimidine;

citrazinic acid;



an aminopyrazole or a pyrazolone derivative of formula



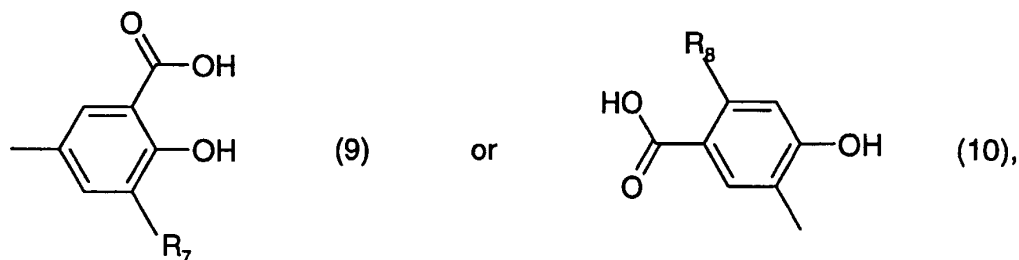
in which

R<sub>4</sub> represents C<sub>1</sub>-C<sub>4</sub>alkyl or CO<sub>2</sub>H,

R<sub>5</sub> represents hydrogen, halogen, C<sub>1</sub>-C<sub>4</sub>alkyl, SO<sub>3</sub>H or CO<sub>2</sub>H and

R<sub>6</sub> represents hydrogen;

a benzoic acid derivative of formula

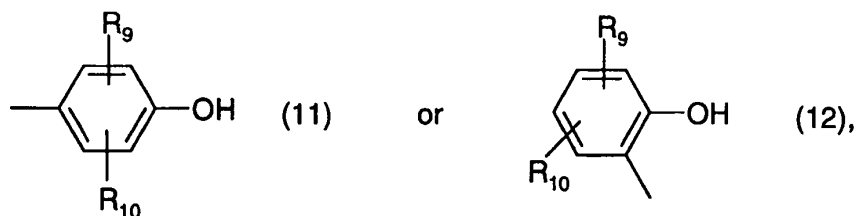


in which

R<sub>7</sub> represents hydrogen or C<sub>1</sub>-C<sub>4</sub>alkyl and

R<sub>8</sub> represents hydrogen or hydroxy or

A<sub>1</sub> and A<sub>2</sub>, each one independently of the other, represent a phenol residue of the formula

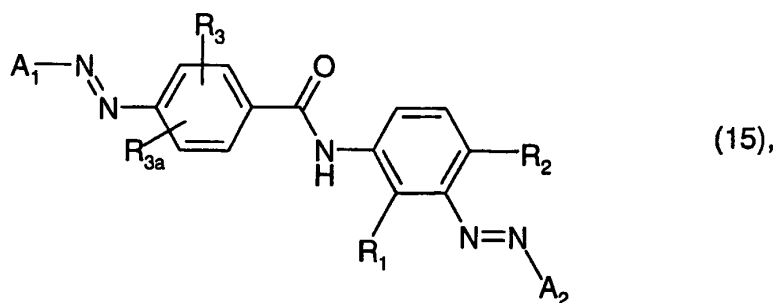


in which

R<sub>9</sub> represents hydrogen, C<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>1</sub>-C<sub>4</sub>alkoxy, hydroxy, halogen or SO<sub>3</sub>H and

R<sub>10</sub> represents hydrogen.

7. A compound of formula



according to claims 1 or 2, in which

R<sub>1</sub> represents hydrogen, C<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>1</sub>-C<sub>4</sub>alkoxy or SO<sub>3</sub>H,

R<sub>2</sub> represents SO<sub>3</sub>H or CO<sub>2</sub>H,

R<sub>3</sub> represents hydrogen, a C<sub>1</sub>-C<sub>4</sub>alkyl group, halogen, hydroxy, C<sub>1</sub>-C<sub>4</sub>alkoxy, carboxy, NH<sub>2</sub> or NHC<sub>1</sub>-C<sub>4</sub>alkyl,

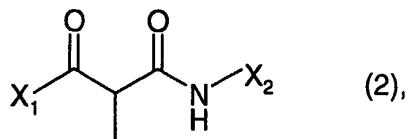
R<sub>3a</sub> represents hydrogen or NH<sub>2</sub> and

A<sub>1</sub> and A<sub>2</sub> are as defined in claim 1.

8. A compound of formula (15), according to claim 7, in which

R<sub>3</sub> and R<sub>3a</sub> both represent hydrogen and

A<sub>1</sub> and A<sub>2</sub>, each one independently of the other, is derived from a coupling component selected from the group consisting of an acetoacetylated amine of the formula



in which

X<sub>1</sub> represents C<sub>1</sub>-C<sub>4</sub>alkyl, and

X<sub>2</sub> represents phenyl, which is unsubstituted, mono-, di- or trisubstituted by SO<sub>3</sub>H, C<sub>1</sub>-C<sub>4</sub>alkyl, hydroxy, C<sub>1</sub>-C<sub>4</sub>alkoxy, halogen or CO<sub>2</sub>H;

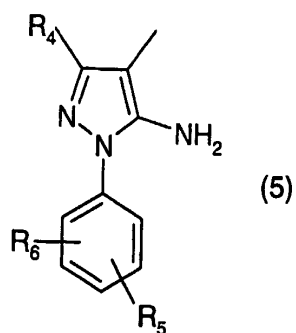
barbituric acid or cyanoiminobarbituric acid;

2,4,6-triaminopyrimidine;

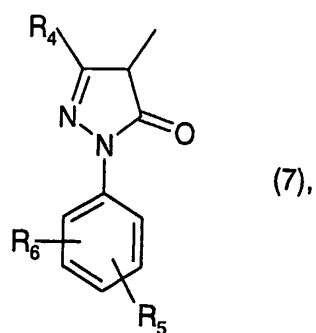
citrazinic acid;

an aminopyrazole or a pyrazolone derivative of formula

- 79 -



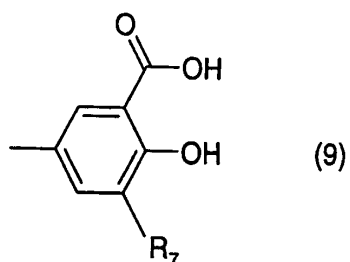
or



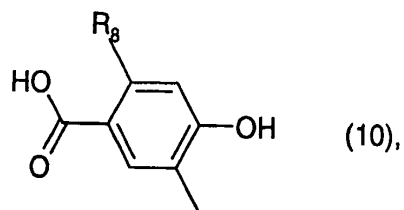
in which

 $R_4$  represents  $C_1$ - $C_4$ alkyl or  $CO_2H$ , $R_5$  represents hydrogen, halogen,  $C_1$ - $C_4$ alkyl,  $SO_3H$  or  $CO_2H$  and $R_6$  represents hydrogen;

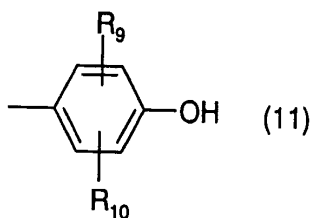
a benzoic acid derivative of formula



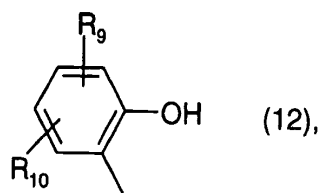
or



in which

 $R_7$  represents hydrogen or  $C_1$ - $C_4$ alkyl and $R_8$  represents hydrogen or hydroxy or $A_1$  and  $A_2$ , each one independently of the other, represent a phenol residue of the formula

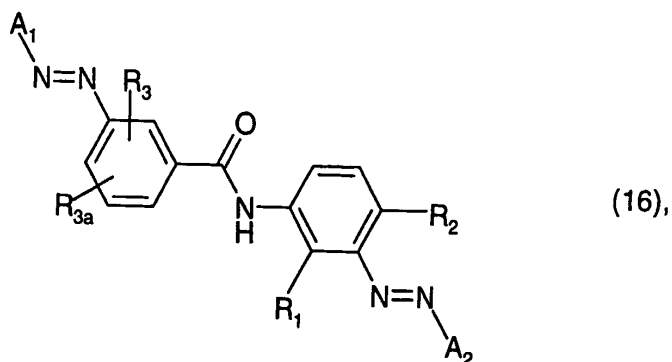
or



in which

 $R_9$  represents hydrogen,  $C_1$ - $C_4$ alkyl,  $C_1$ - $C_4$ alkoxy, hydroxy, halogen or  $SO_3H$  and $R_{10}$  represents hydrogen.

9. A compound of formula



according to claims 1 or 2, in which

$R_1$  represents hydrogen,  $C_1$ - $C_4$ alkyl,  $C_1$ - $C_4$ alkoxy or  $SO_3H$ ,

$R_2$  represents  $SO_3H$  or  $CO_2H$ ,

$R_3$  represents hydrogen, a  $C_1$ - $C_4$ alkyl group, halogen, hydroxy,  $C_1$ - $C_4$ alkoxy, carboxy,  $NH_2$  or  $NHC_1$ - $C_4$ alkyl,

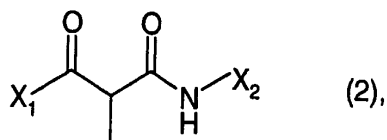
$R_{3a}$  represents hydrogen or  $NH_2$  and

$A_1$  and  $A_2$  are as defined in claim 1.

10. A compound of formula (16), according to claim 9, in which

$R_3$  and  $R_{3a}$  both represent hydrogen and

$A_1$  and  $A_2$ , each one independently of the other, is derived from a coupling component selected from the group consisting of an acetoacetylated amine of the formula



in which

$X_1$  represents  $C_1$ - $C_4$ alkyl, and

$X_2$  represents phenyl, which is unsubstituted, mono-, di- or trisubstituted by  $SO_3H$ ,  $C_1$ - $C_4$ alkyl, hydroxy,  $C_1$ - $C_4$ alkoxy, halogen or  $CO_2H$ ;

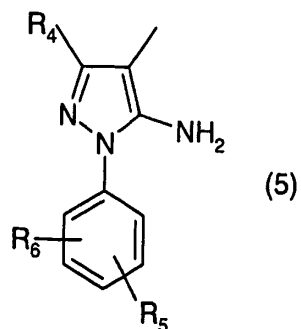
barbituric acid or cyanoiminobarbituric acid;

2,4,6-triaminopyrimidine;

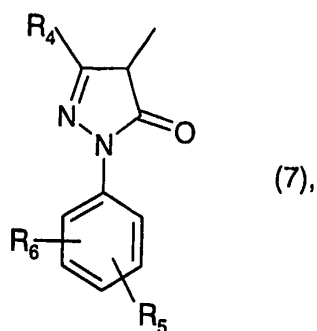
citrazinic acid;

an aminopyrazole or a pyrazolone derivative of formula

- 81 -



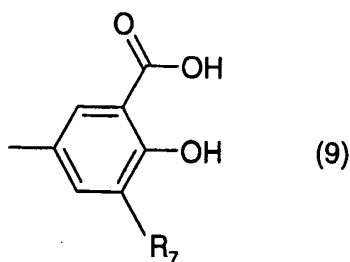
or



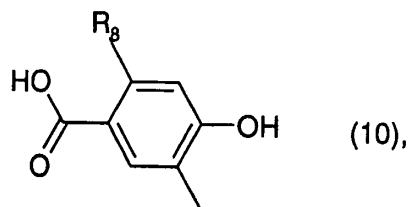
in which

 $R_4$  represents  $C_1$ - $C_4$ alkyl or  $CO_2H$ , $R_5$  represents hydrogen, halogen,  $C_1$ - $C_4$ alkyl,  $SO_3H$  or  $CO_2H$  and $R_6$  represents hydrogen;

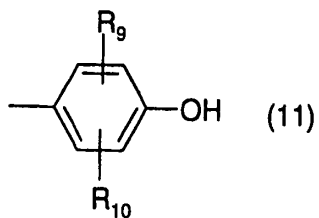
a benzoic acid derivative of formula



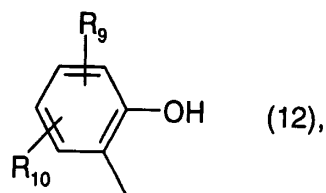
or



in which

 $R_7$  represents hydrogen or  $C_1$ - $C_4$ alkyl and $R_8$  represents hydrogen or hydroxy or $A_1$  and  $A_2$ , each one independently of the other, represent a phenol residue of the formula

or

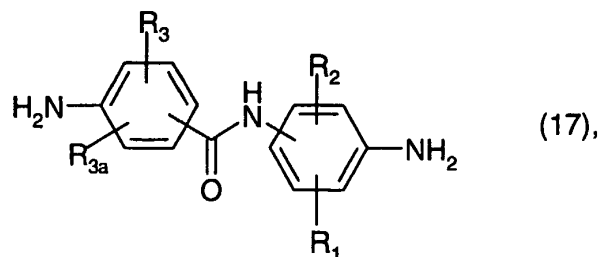


in which

 $R_9$  represents hydrogen,  $C_1$ - $C_4$ alkyl,  $C_1$ - $C_4$ alkoxy, hydroxy, halogen or  $SO_3H$  and $R_{10}$  represents hydrogen.

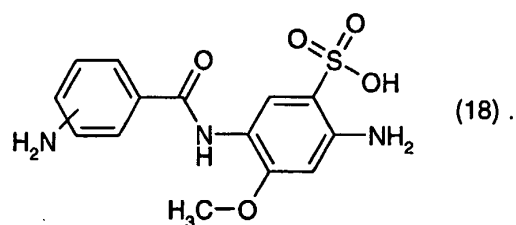
11. A process for the preparation of a compound of formula (1), according to claim 1, by tetrazotisation of a diaminobenzanilide derivative of the formula

- 82 -



in which  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_{3a}$  are as defined in claim 1, and sequential coupling with a coupling component of the formula  $A_1H$  or  $A_2H$ , followed by coupling with a coupling component of the formula  $A_2H$  or  $A_1H$ ,  $A_2$  and  $A_1$  being as defined in claim 1.

12. A compound of the formula



13. A process for the preparation of compound (18), according to claim 12, by reaction of 2-methoxy-4-nitroaniline-5-sulphonic acid with the appropriate nitrobenzoyl halide, followed by reduction of the resulting dinitrobenzanilide.

14. Use of the compound of formula (18), according to claim 12, for the preparation of the appropriate compound of formula (1), according to claim 1.

15. Use of the compound of formula (1), according to claim 1, for dyeing natural or synthetic materials.

16. A solid dye preparation for dyeing paper, comprising a compound of the formula (1) according to claim 1, and, optionally, further auxiliaries.

17. Aqueous solutions for dyeing paper, comprising a compound of the formula (1), according to claim 1, and, optionally, further auxiliaries.

18. Aqueous solutions according to claim 17 containing, as further auxiliaries, solubilizers and/or organic solvents.
19. Paper which is dyed with a compound of the formula (1), according to claim 1, in the form of a solid dye preparation, according to claim 16, or an aqueous solution, according to claim 17.